

Ultrasonic Investigation of Elastic Properties in ZnS:Ce Nanocrystallite

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ABSTRACT

Cerium doped ZnS nanoparticles were prepared by chemical route. The particle size was determined from the X-ray line broadening. Samples were characterized by XRD, FTIR and UV and SEM. The composition was verified by EDAX spectrum. The size of the particles increased as the annealing temperature was increased. The crystallite size varied from 21.7 nm to 25 nm as the calcination temperature increased. Ultrasonic velocity through doped and undoped sample is measured and compressibility is computed. Variation of Compressibility of Zn S: Ce nanofluid with various grain size have been carried out and found that compressibility increases with decrease of particle size. To study the elastic properties of the nano fluid extensively, certain important physical parameters such as adiabatic compressibility, specific acoustic impedance, relative association, intermolecular free length, Rao's constant, Wada's constant etc. are evaluated using ultrasonic velocity and density.

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INTRODUCTION

It is well-known that the optical and electronic properties change dramatically

due to quantum confinement of the charge carriers within the particle. ZnS, which is an important wide band gap semiconductor, has potential applications in electronics and

optoelectronics including light emitting diodes, efficient phosphors in flat-panel displays and photo voltaic devices because of its wide direct band gap 3.77eV^{1,2}. One Dimensional ZnS nano particle have been attracting growing attention because they possess unique properties compared to bulk crystal due to quantum confinement and surface effect.³. Doped semiconductor nanoparticle ZnS:Ce is used as phosphors and also in thin film electroluminescent devices⁴. Recently ZnS nanostructures have shown, a great promise and functional structure nanobuilding blocks in nanoelectronics, nano-optoelectronics and nanolaser^{5,6}. Refinement of XRD data revealed that ZnS nanoparticle in cubic (Sphalerite) phase exhibited structural phase transition under ambient conditions, that exhibited compressibility of ZnS nanoparticle increases substantially as the particle size decreases⁷. ZnS has been used in many military applications requiring mechanical resistance to hostile environment, missile domes and external windows of military aircraft. Since the mechanical properties are crucial for designing such devices there is an increasing interest in the elasticity of nanostructures. The elastic properties of ZnS nanostructures has been investigated that the bulk modulus were decreased with increasing particle size^{8,9}. Band gap energy increases on doping with Ce. The cerium ion doping will change carrier concentration in the ZnS nano particles¹⁰. The dopant sites, defects induced by doping have strong impact on the Structural, Mechanical and Optical properties of ZnS¹¹. Hence, it is interesting to synthesize nanoparticles of ZnS doped with Ce and characterize them and subject

them to Elastic studies. Nanofluids have been of great interest due to their broad applications in different fields¹². The anomalous behavior of ultrasonic velocity in sintered ZnS provides information about the pore size, pore shape and their distribution¹³. Only little information is available about elastic properties of ZnS in the literature and no work has been reported for determining the ultrasonic properties in Ce doped ZnS nanofluid. The ultrasonic velocity measurements are performed for ultrasonic characterization of the prepared fluid.

Aim of this investigation is to measure Ultrasonic velocity through doped and undoped sample and certain important elastic parameters such as Adiabatic Compressibility, Specific Acoustic Impedance, Relative association, Intermolecular free length, Rao's constant, Wada's constant etc. and study their variations with grain size.

EXPERIMENTAL

Nanoparticles of Ce doped ZnS were prepared by chemical co-precipitation method¹⁴. All the chemicals were of AR grade and were used without further purification. For the synthesis of Ce³⁺ doped ZnS, 3g (0.35M) of Zinc Acetate in 40 ml of deionized water-ethanol matrix (equal volumes) and 1.5g (0.39M) of Ce (III) Chloride Hepta hydrate in 10 ml of water were mixed drop by drop. The entire mixture was stirred magnetically at 80°C until a homogeneous solution was stirred. The 3g (1M) of thiourea in 40ml of deionized water ethanol matrix was added to the above mixture. The entire solution was stirred magnetically until a white precipitate was formed. The obtained dispersion was

purified by dialysis against deionized water and acetone several times to remove impurities. Few drops of Tri Ethyle Amine (TEA) is added to the solution to reduce the agglomeration of particles to remove the impurities, including traces of TEA and the original reactants, if any. The wet precipitate was dried in the controlled temperature furnace at 120°C for 2h and thoroughly pulverized.

X-Ray Diffraction (XRD) and Fourier Transform Infrared (FTIR) analyses of these samples were done for their characterization. XRD patterns were recorded on a RigakuC/max-2500 diffractometer using graphite filtered $\text{CuK}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$) at 40 kV and 100 mA with a scanning rate of 8° per min from $2\theta = 5^\circ$ to 80° . The FTIR spectra were recorded in an FTIR spectrometer (Nicolet Magna-750) in the range of 500 cm^{-1} to 4000 cm^{-1} . The

percentage of doped impurity is measured from EDAX spectrum. The Energy Dispersive Analysis of X-rays (EDAX) was done on the sample to ascertain the composition. Scanning Electron Microscopy (SEM) uses electrons to form an image. It is used to show sub-surface defects.

In this investigation, Ultra sound technique was used to measure velocity of the sound. Speed of sound was measured by using a variable path, single crystal interferometer. (Mittal Enterprises, New Delhi). The interferometer cell was filled with the test fluid, and water was circulated around the measuring cell from a thermostat. Ultrasonic velocity was measured with an accuracy $\pm 0.1\%$ and error of measurement $\pm 0.5^\circ\text{C}$ at 303K. The various acoustic parameters are evaluated using ultrasonic velocity, compressibility and density¹².

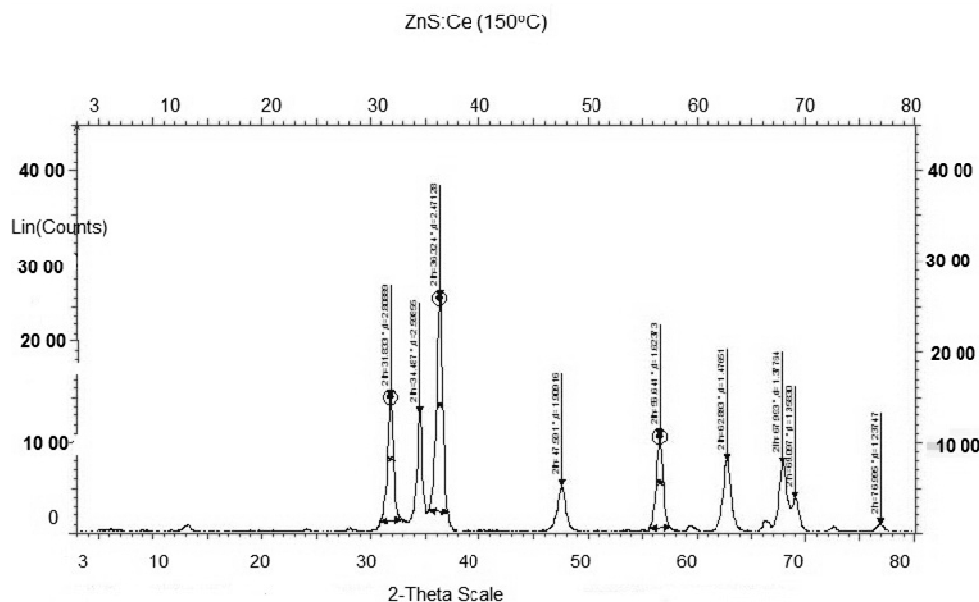


Figure 1(a)

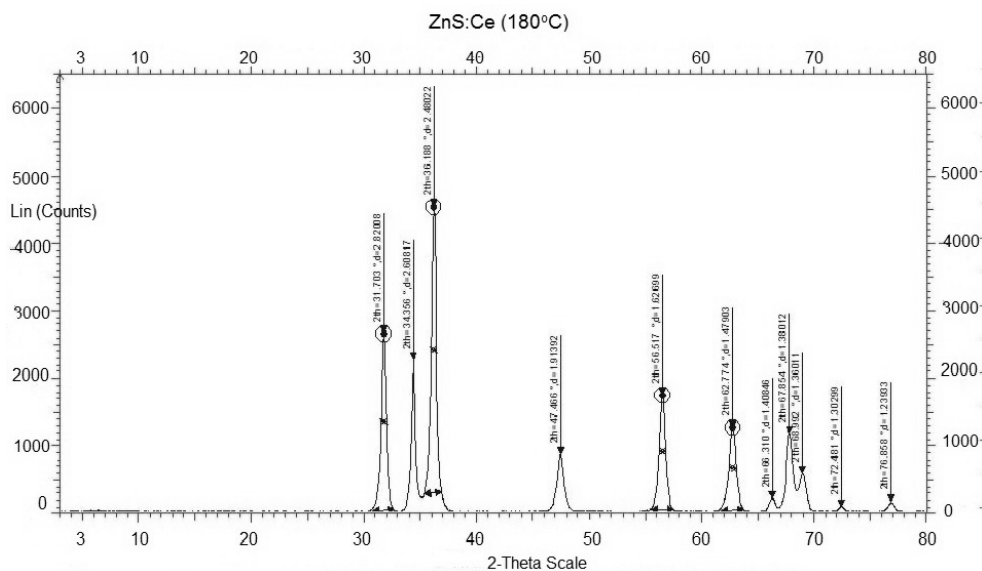


Figure 1(b)

Fig1.(a-b) XRD pattern of ZnS:Ce nanoparticles at 150 and 180°C

Table 1.Variation of Grain size of ZnS:Ce with temperature

Temperature °C	FWHM	$\beta \times 10^3$	2 θ	θ	Particle size(L) nm
150	0.364	6.34	12.875	6.4375	21.7
180	0.312	5.44	13.352	6.676	25

RESULTS AND DISCUSSIONS

XRD Analysis

XRD patterns, Fig.1 [(a)-(b)], of the samples at two different temperatures are carried out. As prepared sample was calcined at 150 and 180°C for 5 h in air atmosphere to ascertain the formation of different nanocrystalline phases. The patterns are compared with Joint Committee for Powder Diffraction Scan (JCPDS) File No. 01-089-7385. Particle Size, are evaluated and tabulated, in Table 1, by the formula^{15,16}, Debye- Scherrer's formula

$$L = K \lambda / \beta \cos \theta$$

(7)

$K=0.89$, λ the X-ray wavelength = 0.154095 Nm, β the full wavelength at half maximum and θ the half diffraction angle. Particles annealed at temperatures 150°C and 180°C have grain sizes 21.7 nm and 25 nm. A continuous increase in the particle size with temperature was observed. According to Ostwald ripening¹⁶ the increase in the particle size is due to the merging of the smaller particles into larger and is a result of potential energy difference between small and large particles and can occur through solid state diffusion.

SEM Image of ZnS:Ce

The morphology, analysis of die/package cracks and fracture surfaces, bond failures, physical defects on the die or package surfaces and dimension of the sample can be studied using SEM. The Scanning electron micrographs of ZnS nanomaterials synthesized under aqueous medium. The orientation growth of ZnS crystal in water is higher¹⁷. Spherical shaped morphology is observed in the micrograph of ZnS: Ce (Fig.2). The SEM pictures exhibit spherical morphology with self aligned prismatic nanoparticles. The morphology of ZnS nanopowder as revealed by FESEM showed nanoparticles of size 15-100 Nm.

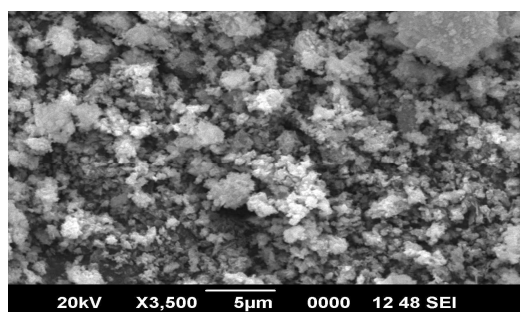


Fig. 2. SEM images of the prepared ZnS:Ce Nanocrystals

FTIR Spectrum of ZnS:Ce

The graph depicted in [Fig.3] represents the percentage variation of transmittance with wave number (cm^{-1}). For ZnS:Ce annealed at 350°C the absorption peaks were observed at 3396.15 cm^{-1} , 1625.88 cm^{-1} , 1545.39 cm^{-1} , 1384.10 cm^{-1} , 1019.87 cm^{-1} , 829.06 cm^{-1} , 675.89 cm^{-1} and 608.40 cm^{-1} . The FTIR measurements are undertaken in order to confirm the formation

of crystalline ZnS nanoparticles and identify any adsorbed species on to the crystal surface. Bands at 418.56 cm^{-1} is assigned to the stretching vibrations of Zn-S^{18} . The stretching frequency of bulk ZnS is 483.72 cm^{-1} . Three intense bands are centered at 1384.08 cm^{-1} , 1023.37 cm^{-1} and 1550.06 cm^{-1} and are attributed to the stretching vibrations of $\text{C}=\text{O}$, $\text{C}=\text{C}$ and C-H groups in acetate species, which suggest it presents as adsorbed species in the surface of nanoparticles. The broad absorption peak centered at 3389.47 cm^{-1} and 2922.47 cm^{-1} corresponds to O-H stretching indicating the existence of water in the surface of nanoparticles^{18,19}.

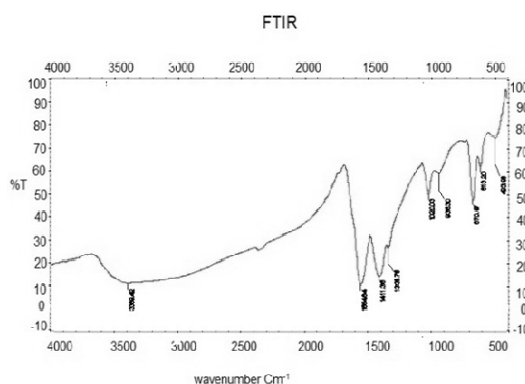


Fig.3 FTIR Spectrum of ZnS:Ce nanoparticle

EDAX (EDS) Spectrum of ZnS:Ce

EDS (EDAX) is a technique used for identifying the elemental composition of the specimen. In EDS spectrum, (Fig.4) each of the peaks is unique to an atom, and therefore corresponds to a single element. The higher a peak in a spectrum, the more concentrated the element is in the spectrum. An EDS spectrum plot not only identifies the element corresponding to each of its

peaks, but the type of X-ray to which it corresponds as well of our sample. About 97.22% of Zn⁺ ion and about 2.28% Ce ion by mass are present in the sample.

Table 2. Measurement of Ultrasonic velocity, Compressibility and Wada’s constant in doped and undoped ZnS:Ce nanofluid.

Fluid	Reading	$\lambda / 2$	Mean λ	Velo. $V=f \lambda$	Compress. $\beta = 1/\rho v^2$ (A ^o)	Wada’s constant $W= (M/\rho)\beta^{-1/7}$ (m ³ /mole) * (10 ⁻⁴)	Relative Association $R_a=(V_o/V_s)^{1/3}$ * (ρ_s/ρ_o)
Ethylene Glycol	5.49 5.401 5.31 5.219 5.129 5.039 4.95 4.86	0.089 0.091 0.091 0.09 0.09 0.089 0.09	0.18	360	69.3	8.165	
Ce doped Zinc Sulphide nanofluid	12.5 12.412 12.328 12.238 12.15 12.066 11.978 11.891	0.088 0.084 0.09 0.088 0.084 0.088 0.087	0.174	348	20.1	4.181	3.723
Undoped ZnS nanofluid	11.797 11.708 11.615 11.528 11.443	0.089 0.093 0.087 0.085	0.177	354	19.51	4.073	3.6664

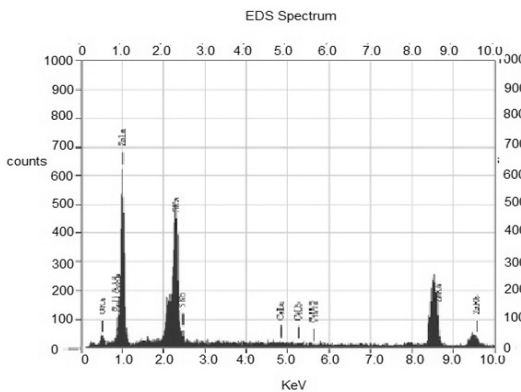


Fig. 4. EDAX Spectrum of ZnS:Ce nanoparticles

Measurement of Ultrasonic velocity

Compressibility and Wada’s constant, Relative Association of Ce doped and undoped ZnS Nanofluids

The ultrasonic velocity is measured using ultrasonic interferometer (Mittel enterprises, F-80 model) at a standard frequency of 2 MHz with an accuracy of 1m/s. The principle used in the measurement of velocity²⁰ is based on the accurate determination of the wave length in the medium. Ultrasonic waves of known

frequency are produced by a quartz plate fixed at the bottom of the cell. The waves are replaced by a movable metallic plate kept parallel to the quartz plate. If the separation between these plates is exactly a whole multiple of the sound wavelength, standing waves are formed in the medium. The acoustic resonance gives rise to an electrical reaction on the generator driving the quartz plate and the anode current of the generator becomes maximum. If the distance is now increased or decreased and the variation exactly one half wavelength or multiple of it, anode current again becomes maximum. From the knowledge of wavelength the velocity of ultrasonic wave can be obtained by the relation. The behaviour of ultrasonic velocity can be understood with its related quantities. The ultrasonic velocity is well related to bulk modulus (B), compressibility (k), and density(ρ) of the medium²⁰. Hence, the enhancement in velocity by the dispersion of nanoparticles is due to change in density, compressibility, bulk modulus of the

nanoparticle suspension with volume fraction. The velocities of the present nanofluids are found greater than the velocity in pure matrix state, which indicates that by the dispersion of solid particles, there is a change in density and bulk modulus.

2gm of doped and undoped ZnS is dissolved in 5ml of Ethylene Glycol and taken in the cell. The velocity of ultrasonic waves of frequency 2MHz is found out. The density ZnS:Ce nanofluid, undoped ZnS nanofluid, and ethylene glycol have been carried out $\rho = 4.18 \times 10^3 \text{ Kg/m}^3$ and as, $\rho = 4.090 \times 10^3 \text{ Kg/m}^3$ and $\rho = 1.1132 \times 10^3 \text{ Kg/m}^3$. The Compressibility and Wada's constant of ZnS increases on doping with Ce. The result indicate that ZnS:Ce material are easy to deform but difficult to compress. The elasticity of Zn S increases with increase in mole percentage of CeO₂. In order to explain the high value of elastic constant in ZnS doped with Ce, the chain entanglement mechanism in ZnS with the structural modification by alkaline earth ions was used¹⁵.

Table 3. Variation of Compressibility, Wada's constant, Bulk modulus of ZnS:Ce nanofluid with particle size

Temperature °C	Particle size(L) Nm	Ultrasonic velocity (m/s)	Compressibility β (A°)	Wada's constant $\times 10^{-4} \text{ m}^3/\text{mole}$	Bulk Modulus $K=1/\beta$ (10^{10})m
150	21.7	348	20.1	4.181	0.0497
180	25	359.9	18.46	4.073	0.0541

Table 4. Variation of Rao's constant, Acoustic impedance, free length of ZnS:Ce nanoparticle with particle size

Temp(°C)	Particle size (nm)	Rao's constant $R = (M/\rho) V^{1/3}$ (10^{-4}) (M3/mole)(m/s) ^{1/3}	Acoustic impedance $Z = V \times \rho$ (10^4)(kg/m ² /sec)	Free length $L_f = K(\beta)^{1/2}$ (A°)
150	21.7	1.639	145.46	0.922
180	25	1.658	150.48	0.884

An increase in bulk modulus, Table 3, or decrease in compressibility is attributed to the fact that strong cohesive interaction forces act among the molecules and atoms after the dispersion of ZnS nanoparticles in the ethylene glycol. The variation of Rao's constant with temperature is as shown in Table 4. The Rao's constant increases with temperature and particle size. The molecules of liquid are not closely packed and as such there is always some free space between them.

The Wada's constant changes with temperature are shown in Table 3. The constant decreases with rise of temperature and particle size. Which shows that solute solvent molecules are coming close to each other and the space between them is decreasing with rise in temperature. This supports to the strong solute-solvent interaction in liquid solution¹³. The Wada's constant increases with Ce impurity doping as depicted in Table 2. It is a measure of change in internal energy of liquid solution as it undergoes a very small isothermal change. It is a measure of cohesive or binding forces between the solute and solvent interaction¹². Variation of acoustic impedance with temperature and particle size are depicted in the Table 4. Acoustic specific impedance Z increases with increase in temperature and particle size which indicates that there is strong interaction between solute and solvent¹². Intermolecular free length (L_f) is one of the important acoustic properties to study the intermolecular interactions. L_f decreases with increasing particle size, Table 4, shows that there is enhanced molecular association which is confirmed by values of viscosity which increases with concentration²⁰.

Relative Association R_a of the samples, Table 2, increases on doping the sample with Ce. Relative association is the measure of extent of association of the component in the mixture. The value of relative association increases with doping indicating strong interionic interaction²⁰.

CONCLUSIONS

The structure and composition of Ce doped ZnS nanoparticles were determined by XRD, FTIR, SEM and EDAX spectra analyses. Ce doped ZnS nanoparticles have been prepared by chemical co-precipitation method. The XRD results indicated that the particle size of nano ZnS:Ce is much small as compared to that of pure nano ZnS and decreases with the Cerium loading. From the XRD results, it is clear that as temperature increases, particle size also increases. Absorption peaks in the FTIR spectrum of ZnS:Ce with different particle size were explained. Ultrasonic velocity through doped and undoped sample is measured and compressibility is computed. The compressibility is found to be increased. Also variation of compressibility of Zn S:Ce nanofluid with various grain size have been carried out and found that compressibility increases with decrease of particle size. To study the elastic properties of the nano fluid certain important physical parameters such as adiabatic compressibility, specific acoustic impedance, relative association, intermolecular free length, Rao's constant, Wada's constant etc. are evaluated using ultrasonic velocity, density. The variations in these Acoustic parameters with grain size and temperature are reported.

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